Effect of Solute Size and Solute-Water Attractive Interactions on Hydration Water Structure Around Hydrophobic Solutes

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Using Monte Carlo simulations, we investigate the influence of solute size and solute-water attractive interactions on hydration water structure around spherical clusters of hexagonally close-packed methanes and single hard-sphere (HS) solute analogues of these clusters, ranging in size from a single methane to that comparable to a small globular protein. We obtain quantitative results on the density of water molecules in contact with the HS solutes as a function of solute size for HS diameters between 0.6 and 3.3 nm. Analysis of these results based on scaled-particle theory yields a hydration free energy/surface area coefficient equal to 14 kcal/(mol·nm^2), independent of solute size, when this coefficient is defined with respect to the van der Waals surface of the solute. The same coefficient defined with respect to the solvent-accessible surface decreases with decreasing solute size for HS diameters less than ~2 nm. We also find that solute-water attractive interactions play an important role in the hydration of the methane clusters. Water densities in the first hydration shell of the three largest clusters are greater than bulk water density and are insensitive to the cluster size. In contrast, contact water densities for the HS analogues of these clusters decrease with solute size, falling below the bulk density of water for the two largest solutes. Thus, the large HS solutes dewet, while methane clusters of the same size do not.